Integrated anode structure for passive direct methanol fuel cells with neat methanol operation

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HIGHLIGHTS

- An integrated anode structure based on a microporous titanium plate is developed.
- The maximum power density of 40 mW cm^{-2} for passive DMFCs is obtained at 25 °C.
- The volumetric energy density of 489 Wh L^{-1} is obtained with neat methanol.
- Over 90 h of operation is conducted with no obvious performance degradation.

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ABSTRACT

A microporous titanium plate based integrated anode structure (Ti-IAS) suitable for passive direct methanol fuel cells (DMFCs) fueled with neat methanol is reported. This anode structure incorporates a porous titanium plate as a methanol mass transfer barrier and current collector, pervaporation film for passively vaporizing methanol, vaporous methanol cavity for evenly distributing fuel, and channels for carbon dioxide venting. With the effective control of methanol delivery rate, the Ti-IAS based DMFC allows the direct use of neat methanol as the fuel source. In the meantime, the required water for methanol—oxidation reaction at the anode can also be fully recovered from the cathode with the help of the highly hydrophobic microporous layer in the cathode. DMFCs incorporating this new anode structure exhibit a power density as high as 40 mW cm^{-2} and a high volumetric energy density of 489 Wh L^{-1} operating with neat methanol and at 25 °C. Importantly, no obvious performance degradation of the passive DMFC system is observed after more than 90 h of continuous operation. The experimental results reveal that the compact DMFC based on the Ti-IAS exhibits a substantial potential as power sources for portable applications.

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1. Introduction

With the rapid development of portable electronic products, such as smart phones, laptop computers and PDA, there is an urgent demand for the high specific energy of portable power sources [1–5]. The direct methanol fuel cell (DMFC) has been considered as an attractive candidate to replace the existing batteries in portable devices because of their unique properties such as instantaneously refueling, environmental friendliness, and high specific energy [6,7]. To date, although much progress has been made for the development of the DMFCs, technical challenges such as compact structures for maximizing energy density still need to be addressed for portable applications.

To issue a high energy density of the DMFCs, it's desirable to achieve a stable operation with neat methanol. Since the rate of methanol crossover is generally proportional to the methanol concentration at the anode catalyst layer, a controllable rate of methanol delivery at the anode is a crucial issue to reduce the methanol crossover. Actually, it has been confirmed that a passive mass transport barrier between the anode catalytic layer and the fuel reservoir can greatly inhibit methanol crossover, and thus realizing high-concentration operation. Abdelkareem and Nakagawa [8] demonstrated that a passive DMFC with a porous graphite plate as a support can significantly reduce the methanol crossover, leading to the DMFC operation with highly concentrated methanol. A maximal power density of 24 mW cm^{-2} is reported

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with the supply of 16 M of methanol at room temperature. Other novel materials and new structures such as hydrogels [9], flexible graphite plate [10], microfluidic-structured anode flow field [11], two parallel flow channel plates [12] were also developed to control the methanol diffusion rate. However, the direct feeding of neat methanol for passive DMFCs cannot still be realized until methanol can be passively vaporized by introducing a pervaporation film (PVF) located between the fuel cartridge and the anodic current collector by Ren et al. [13,14]. Furthermore, Xu et al. [15] adopted four layers of porous PTFE membrane as a PVF together with one porous PTFE sheet (25 μm pore size and 1.59 mm thickness) and a platinum-coated niobium expanded metal mesh to control the mass transfer rate of methanol to the anode catalyst layer for neat methanol operation. Based on the structure optimization, a peak power density of 34 mW cm^{-2} at room temperature can be yielded.

The effective management of water is another important issue for the passive DMFCs with neat methanol operation [16]. It's known that 1 mol of water is required for 1 mol of methanol fully being oxidized at the anode. Furthermore, the proton conductivity of Nafion$^®$ membranes is also strongly dependent on its water content. Therefore, it's indispensable to push part or whole of the produced-water at the cathode side backflow across the membrane to the anode side, which is usually achieved by the hydraulic pressure buildup within the hydrophobic microporous layer in the cathode [17,18]. As a result, the methanol concentration in the anode catalyst should be maintained at an appropriate level (e.g. less than 2 M). In addition, there is a close interaction between the feed methanol concentration and water effective management. In the case of different methanol mass transfer rates at anode, water effective management must be accommodated for the DMFCs with a high performance operation.

The above literature survey demonstrates that the use of a PVF together with relatively small open ratio of anode current collectors as a methanol blocker as well as a hydrophobic microporous layer at the cathode as water back-diffusion layer is an effective solution for the passive DMFCs operating with highly concentrated methanol. However, it is worth noting that the related structures have either several layers to enable the control of methanol mass transfer or incapability to suppress methanol crossover, aiming at the direct feeding with neat methanol. Moreover, the miniature passive DMFCs as power sources for portable applications are desirable with a compact structure, high performance, and stable operation. Therefore, we provide an integrated anode structure based on a microporous titanium plate (Ti-IAS), which incorporates a porous titanium plate as a methanol mass transfer barrier and current collector, PVF for passively vaporizing methanol, vaporous methanol cavity for evenly distributing fuel, and channels for carbon oxide venting. With such a systematical simplification, a stable operation DMFC with high performance could be realized, and such a passive DMFC demonstrates a substantial potential for portable applications.

2. Experimental

2.1. Preparation of a membrane electrode assembly (MEA)

The electrolyte membranes were the traditional Nafion$^®$ series membranes (DuPont) and the pre-treatment procedure involved three sequential boiling steps described at elsewhere [19]. If not specified, Nafion$^®$ 115 membrane will be taken as the electrolyte membranes in the following experiments. A slurry which consisted of Vulcan XC-72 carbon and PTFE emulsion (20 wt.%) was blade-coated onto the carbon paper (TGPH060, 20 wt.% PTFE,

Toray) to form the anodic microporous layer (MPL). The XC-72 carbon loading was ca. 1 mg cm^{-2}. For the preparation of cathodic MPL, a slurry consisting of Vulcan XC-72 carbon and PTFE emulsion (40 wt.%) was first blade-coated onto the carbon paper (TGPH060, 20 wt.% PTFE, Toray), then a highly-hydrophobic MPL that consisted of a mixture of 50 wt.% PTFE emulsion and KB-600 carbon particles was fabricated on the surface of the as-prepared MPL. The carbon loading was ca. 1 mg cm^{-2}, respectively. Then, the ink comprised of Pt–Ru black (Johnson Matthey) and carbon supported Pt (60 wt.% Pt, Johnson Matthey) mixed with 20 wt.% Nafion was blade-coated on the surface of the as-prepared diffusion layer as the catalyst layer at the anode and the cathode, respectively. The metal loading of the electrode was ca. 4 mg cm^{-2}. Finally, the well-treated membrane was sandwiched between two electrodes by a hot-pressing process at 130 °C and 6 MPa for 3 min to form an MEA unit with an active geometric area of 4 cm^2.

2.2. Fabrication of the integrated anode structure and cell assembly

This anode structure incorporates a microporous sintered titanium plate, PVF, vaporous methanol cavity, and carbon oxide vent channels, which is shown in Fig. 1(a). An indentation on the back of the microporous sintered-titanium plate was engraved to form a vaporous methanol cavity together with the PVF. Moreover, the carbon dioxide vent channels were also engraved at the edge of the titanium plate. In this study, three kinds of microporous titanium plates with the same thickness of 1.5 mm have the approximate porosity of 40% and different average pore sizes of 35, 75, and 100 μm, which was measured by the capillary flow porometer (Porolux 1000, Germany).

A schematic diagram of the DMFC system based on the Ti-IAS is shown in Fig. 1(b). The MEA was sandwiched between the titanium based cathode current collector and the integrated anode structure. The surface of current collectors was sputtered with a thin layer of gold to reduce the contact resistance between the current collector and the diffusion layer. The open ratio of cathode current collector is 75%. Air is supplied to the cathode catalyst layer only by self-diffusion.

2.3. Electrochemical characterizations

The polarization performance of the passive DMFCs was characterized by an Arbin fuel cell testing system (Arbin Instrument Inc., USA). Each data point was recorded after 180 s waiting time. All the tests were performed at 24–25 °C and with the relative humidity of 30–40%. The as-prepared MEA was activated under ambient conditions by immersed into 2 M methanol solution for 24 h before evaluation.

Methanol crossover and anode polarization behavior were measured by using a Solartron SI2610 testing system in a linear scan voltammograms (LSVs) mode at a scan rate of 20 mV s^{-1}. During the test, the cathode was fed with humidified N$_2$ and H$_2$ while neat methanol was supplied to the anode, respectively.

3. Results and discussion

3.1. Effect of the different Ti-IASs on polarization performance

The surface morphology of three kinds of naked microporous titanium plates is shown in Fig. 2. The surfaces are very smooth, dense and crack-free. However, the compactness within the microporous surface varies considerably, which was characterized by the mean pore diameter. Fig. 3 compares the cell performance of the Ti-IAS based DMFCs with different pore sizes at neat methanol
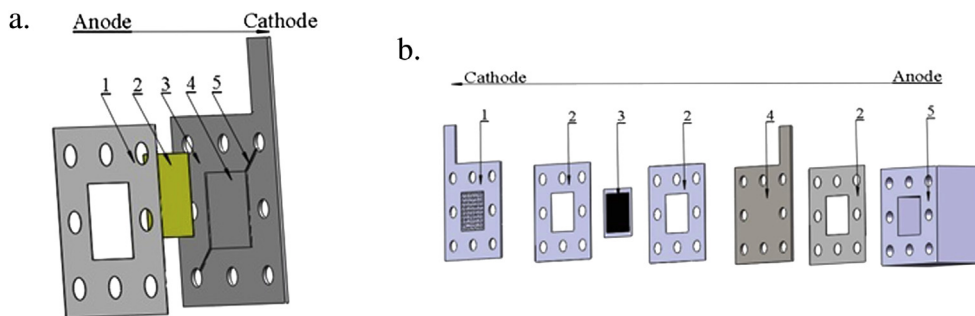
Fig. 1. Schematic of a passive DMFC based on the Ti-IAS including (a) a detailed drawing of the Ti-IAS: (1) PTFE gasket; (2) pervaporation film; (3) microporous titanium plate; (4) vaporous methanol cavity; (5) carbon oxide vent channel; and (b) assembly of the cell: (1) cathode current collector; (2) PTFE gasket; (3) MEA; (4) Ti-IAS; (5) fuel cartridge.

operation. In the case of the same thickness and porosity of the microporous titanium plates, the mean pore diameters have a great influence on the cell polarization performance as a result of controlling the methanol mass transfer rates. The polarization curves at the low current density range (e.g. less than 20 mA cm^{-2}) do not show too much difference among the three kinds of integrated anode structures. With the increase of the current density, the voltage of the DMFC based on Ti-IAS with the pore size of 35 μm tends to drop sharply in comparison with the other two structures, indicating that the methanol mass transfer resistance would be much larger than that of the other two plates. Moreover, the Ti-IAS with the porous size of 75 μm gains the maximum power density. Although that the larger the mean pore size, the higher the limiting current density under circumstance of the same porosity and thickness, the polarization performance has other influence factors such as methanol crossover. It has been reported that the open circuit voltage (OCV) represents the degree of methanol crossover [20]. When the pore sizes increase from 35 to 75 μm, and then to 100 μm, the OCV varies from 0.56 to 0.51 V and then to 0.49 V, indicating that the most serious methanol crossover for the Ti-IAS with the pore size of 100 μm. Furthermore, the highest peak power density of 40 mW cm^{-2} was yielded as Ti-IAS with the pore size of 75 μm was implemented. It's obvious that the methanol mass transfer rate at the anode can be effectively controlled by the integrated anode structure, and thereby methanol crossover can be greatly suppressed. Moreover, in the case of Ti-IAS with the pore size of 75 μm, a relatively good balance between reduction of methanol crossover and maintenance of sufficient methanol supply to the anode catalyst layer in a passive DMFC fed with neat methanol can be realized.

### 3.2. Influence of the different Ti-IASs on the methanol crossover

It's well known that reducing the methanol crossover is very critical for a DMFC at a highly concentrated methanol operation. It's a result of the interactions between confinement of methanol anode mass transport and backflow of water from the cathode to the anode. Moreover, methanol crossover is closely related to the operational state of a DMFC [21]. Therefore, in the following, the methanol crossover rate in a work state is characterized by an equivalent current density of methanol oxidation [22]. The methanol permeation through the membrane is mainly dominated by molecular diffusion. Therefore, when the current density and the methanol concentration in the anode catalyst layer are not too high, the methanol-crossover current density can be determined by [23]:

$$i_\text{c} = i_\text{c,ocv}\left(1 - \frac{i}{i_\text{lim}^\text{M}}\right) \tag{1}$$

where i_c is the equivalent methanol-crossover current density; $i_\text{c,ocv}$ the equivalent methanol-crossover current density under the open circuit condition; i the discharging current density, and i_lim^M denotes the anode limiting current density caused by methanol transport limitation.

Fig. 4 shows the methanol-crossover current density (a) and the anode limiting current density (b) with neat methanol supplied. The equivalent methanol-crossover current density (i_c) can be calculated according to the above equation. When the mean pore size varies from 100 μm, 75 μm, to 35 μm, the corresponding equivalent methanol-crossover current density decreases from 148.6, 83.4, to 43.8 mA cm^{-2} at a given current density of 100 mA cm^{-2}. It's obvious that the variation of the microporous size within the Ti-IAS is an effective way to control the methanol mass transfer rate at the anode, and thereby suppress the methanol crossover. However, although the DMFC based on the Ti-IAS with the pore size of 35 μm has the lowest methanol-crossover current density, the polarization performance is also the lowest among the three kinds of Ti-IASs. On the other hand, the Ti-IAS based DMFC with the pore size of 75 μm gains the highest polarization performance in the case of the anode limiting current densities at ca. 180 mA cm^{-2}. Therefore, it is crucial to realize the tradeoff between reduction of methanol crossover and maintenance of sufficient methanol supply to the anode catalyst layer in a passive DMFC fed with neat methanol, which is also proven by the results shown in
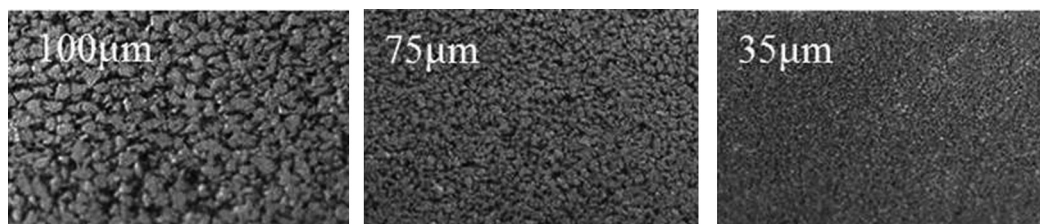
**Fig. 2.** Surface morphology of the three kinds of sintered microporous titanium plate.
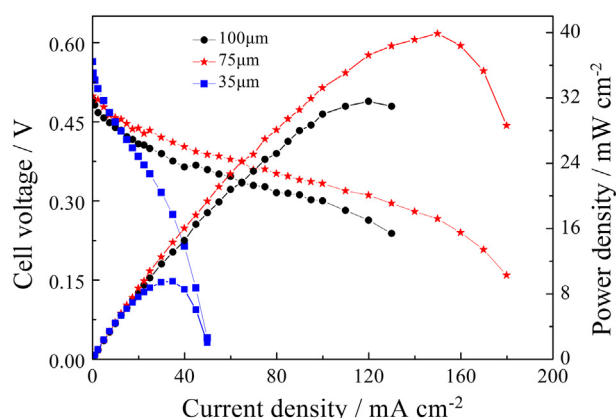
Fig. 3. Performance comparison of the DMFCs based on the Ti-IAS with different mean porous diameters. The DMFCs were operated with neat methanol.

Fig. 3. The Ti-IAS based DMFC with the pore size of 75 μm attains a relatively good balance between the lower methanol crossover and sufficient anode methanol supply.

3.3. Performance comparison of DMFCs between the Ti-IAS based and the conventional structure

For the purpose of comparison, we firstly measured the performance of the DMFC with the conventional anode structure fed with diluted methanol solutions. The polarization curves and the
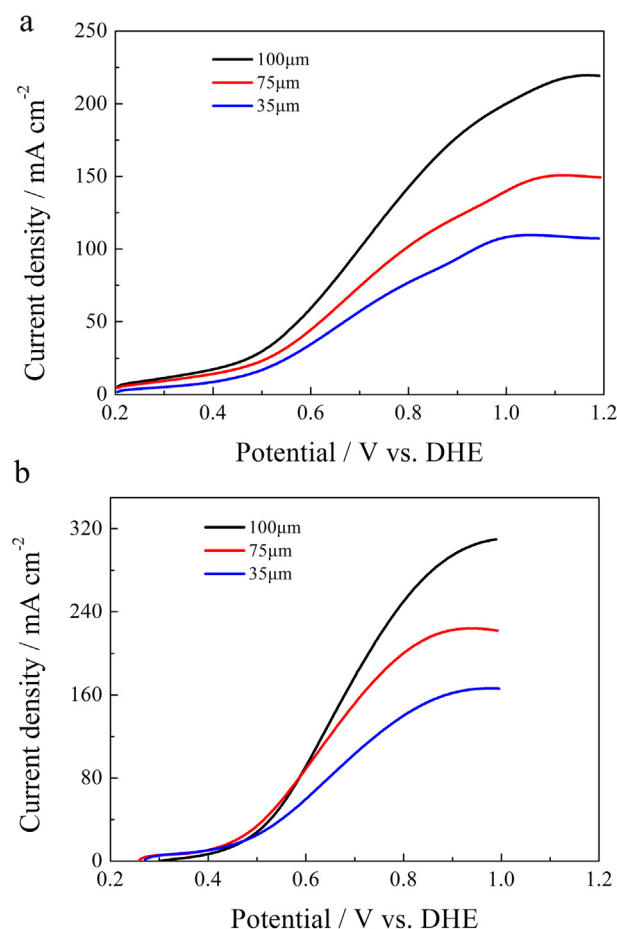
Fig. 4. LSV curves of methanol oxidation on the anode (a) and cathode due to methanol-crossover (b) at a scan rate of 20 mV s^{-1}.

power densities with various methanol concentrations are presented in Fig. 5. It is seen that the peak power density reaches the highest value of 27 mW cm^{-2} at 4 M methanol. This result can be explained as follows: when the feed methanol concentration is too low, the rate of methanol transport to the anode catalyst layer becomes too low, resulting in a larger mass transport polarization. However, too high methanol concentration will lead to a higher rate of methanol crossover. Moreover, the permeated methanol reacts with oxygen and generates more liquid water, which would exacerbate the water flooding in the cathode, and thereby decrease the cell performance further. Therefore, the methanol solution at 4 M is the optimal concentration for a traditional DMFC at a passive mode operation. In the following, the performance comparison of the Ti-IAS based DMFCs with the traditional structure is carried out. It is clearly seen that the Ti-IAS based DMFCs at the neat methanol operation outperforms most that with the traditional structure fed with 4 M methanol aqueous solution. The peak power density for the Ti-IASs based DMFC can be achieved as high as 40 mW cm^{-2}, which is much higher than that of the traditional DMFC with 27 mW cm^{-2}. The reason can be mainly ascribed to the effective suppression of methanol crossover when the DMFC was directly fueled with neat methanol. The neat methanol was firstly vaporized by the PV film [24,25]. The porous titanium plate adjacent to the PV film then played a key role in controlling the mass transfer rate of the vaporized methanol, thereby reducing the methanol crossover greatly.

As is known to all, it is very important for a DMFC with a high volumetric energy density for portable applications. The volumetric energy density of the DMFC can be calculated from

$$Ev = \frac{\text{Discharging energy (W h)}}{\text{Methanol solution volume (L)}} = \frac{V \int_0^T i(t)\mathrm{d}t}{V_M} \qquad (2)$$

where Ev is the volumetric energy density, V is the working voltage, T the total discharging time, $i(t)$ the transient discharging current density, and V_M the volume of the feed methanol solution.

Fig. 6 shows evolution of the current density versus time when the DMFCs were discharged at a constant voltage of 0.3 V with the volume of methanol solution at 3.0 mL. It can be seen that after injecting the fuel, the discharging current density of the traditional DMFC fed with 4 M methanol aqueous solution continuously declines with time due to the consumption of methanol. On the contrary, for the Ti-IAS based DMFC at neat methanol operation, there merely exists a slightly decrease in the current density within
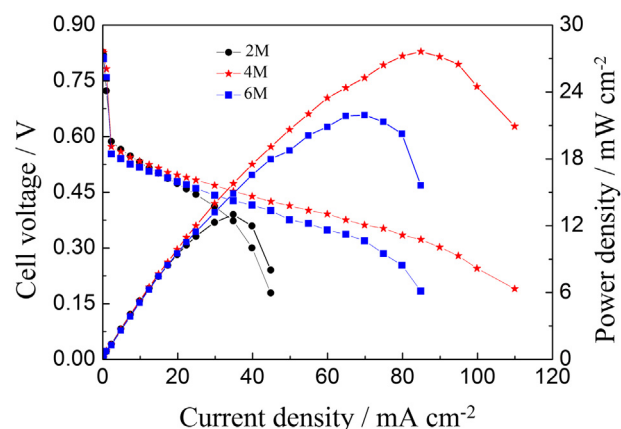
Fig. 5. Polarization performance of the conventional DMFCs fed with diluted methanol solutions.
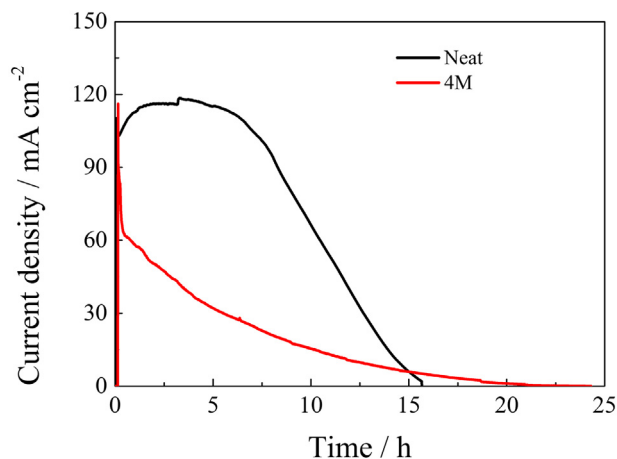
Fig. 6. Transient discharging curve of the passive Ti-IAS based DMFCs at a constant voltage of 0.3 V fueled with 3.0 mL of methanol solution.

the initial 6 h, which mainly attributes to the good balance between the reduction of methanol crossover and sufficient supply of methanol. After discharging for ca. 6.5 h, the current density starts to continuously decrease toward zero due to methanol starvation in the fuel cartridge. According to the Equation (2), the volumetric energy density of the Ti-IAS based DMFCs at neat methanol operation is ca. 489 Wh L^{-1}, which is approximately three times higher than that of the traditional DMFC fed with 4 M methanol aqueous solution (i.e. 164 Wh L^{-1}).

3.4. Effect of Nafion® membrane thickness

The thickness of Nafion® membrane as proton-conductive membrane has a significant influence on water backflow, cell internal resistance and methanol crossover. More importantly, the maintenance of the local methanol concentration in the anode catalyst layer at an appropriate level requires both the control of methanol mass transport at the anode and backflow of water from the cathode. Moreover, there is a close interaction between them. Therefore, when the integrated anode structure is employed to control the methanol mass transport, the corresponding electrolyte membrane should be also accommodated. In the case of a highly hydrophobic microporous layer at the cathode, in the following, the effect of the membrane thickness on the Ti-IAS based DMFC performance was investigated.

Fig. 7(a) shows the variations of the cell performance when using the different electrolyte membranes. It can be seen that Nafion® 115 membrane based DMFCs gains the higher peak power density of 40 mW cm^{-2} than that with the other two kinds of membranes (32 mW cm^{-2} with Nafion® 117, and 31 mW cm^{-2} with Nafion® 212). There are two reasons for the performance improvement in Nafion® 115 membrane. In the first place, compared to Nafion® 112 membrane, the methanol crossover can be further reduced. The thinner the membrane, the more serious the methanol crossover would be. Secondly, it is shown in Fig. 7(b) that the internal resistance of Nafion® 115 membrane is ca. 360 mΩ cm^2, which is lower than that of Nafion® 117 membrane. Moreover, the internal resistance of Nafion® 117 increases from 400 to 441 mΩ cm^2 as the current density increases while the other membranes remain almost constant. The reason may be ascribed to the insufficient hydration within the Nafion® 117 membrane. The internal resistance of Nafion® series membrane is highly dependent on the degree of hydration. The thinner Nafion® membrane, the lower the internal resistance will be. In addition, thin membrane benefits for water backflow from the cathode to the anode.
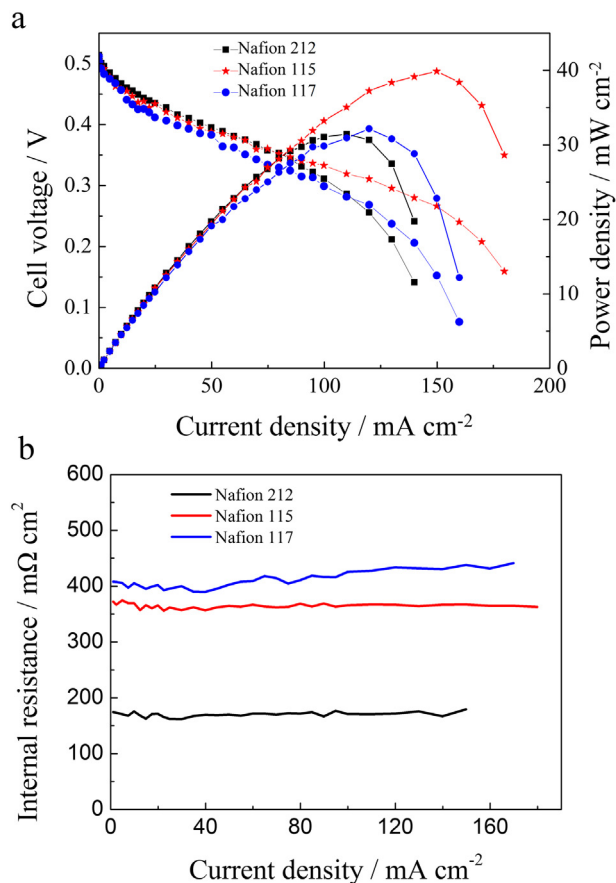

Fig. 7. Variations of polarization curves (a) and internal resistance (b) of the passive DMFCs with different Nafion® membranes.

Therefore, Nafion® 115 membrane gains a good tradeoff between water backflow and methanol crossover in the passive DMFC fed with neat methanol, which would be more suitable for the TI-IAS based DMFCs with high performance operation.

3.5. Durability test

Based on the design and optimization of the integrated anode structure, the as-prepared passive Ti-IAS based DMFC was continuously run for a long-term stability test. Fig. 8 shows the transient
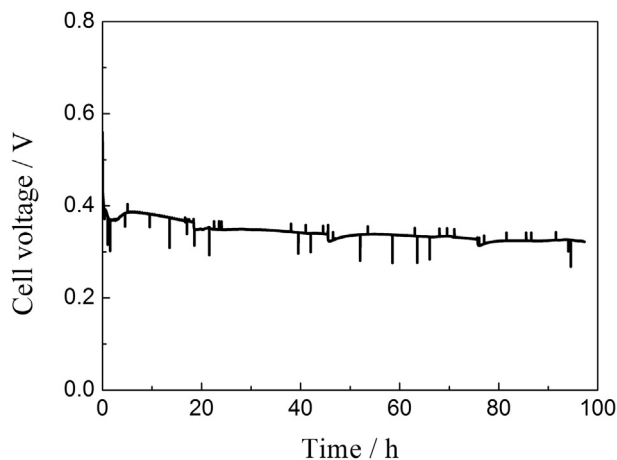

Fig. 8. Durability test of the passive Ti-IAS based DMFC at a current density of 40 mA cm^{-2} with neat methanol as fuel.

evolution of cell voltage for more than 90 h under a constant current density of 40 mA cm^{-2} at neat methanol operation. In the course of the continuous operation, the cell voltage has somewhat fluctuations when neat methanol was refilled to the fuel cartridge. However, it's clear that there is no evidence of permanent performance degradation, indicating that such an integrated anode structure based passive DMFC has a promising capability for stable operation in the case of direct feed neat methanol.

4. Conclusions

An integrated anode structure based on microporous titanium plate suitable for passive DMFCs operating with neat methanol was developed, which incorporated a porous titanium plate, PVF, vaporous methanol cavity, and carbon oxide vent channels. The pore size of microporous titanium plate at 75 μm is preferable as a result of a good tradeoff between reduction of methanol crossover and sufficient supplement of methanol at the anode. Based on the optimization of the structure parameters, a passive DMFC based on the Ti-AIS at neat methanol operation yields a very high power density of 40 mW cm^{-2}. Furthermore, the DMFC after more than 90 h continuous operation at a constant current density of 40 mA cm^{-2} shows no evident performance degradation. By taking advantage of such an integrated anode structure, the polarization performance, operational stability, and even structure compactness of the passive DMFC at neat methanol operation have been substantially improved.

Acknowledgments

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